

## ***Interactive comment on “Continuous measurements of methane mixing ratios from ice cores” by C. Stowasser et al.***

**C. Stowasser et al.**

stowasser@nbi.ku.dk

Received and published: 7 April 2012

Answer to B. Vaughn's (Referee) comment on amtd-5-211-2012

We thank B. Vaughn for his careful examination of our manuscript and his many useful comments.

**1**

*B. Vaughn: Incorporate the changes recommended by Eugster and Referee #2.*

C584

Stowasser et al.: Done (see author's replies to comments of referees #1 and #2)

**2**

*B. Vaughn: Page 215. When describing the performance of the gas extraction module as being dependent on the pressure gradient over the hydrophobic membrane, it is not entirely clear from the text as to how this was achieved. Down-stream pressure control within the cavity is explained, but (unless I missed it), not within the micro-module. For example, do pressure pulses from the peristaltic pump interfere with the pressure regime in the gas extraction system, or is that not a problem? A brief explanation would help.*

Stowasser et al.: The downstream pressure control of the cavity does also control the pressure at the hydrophobic membrane. Variations in the water to gas ratio introduce p-fluctuations at the membrane. Thus the pressure stabilization at the membrane is not as precise ( $700 \pm 20$  mbar) whereas the cavity pressure is controlled to set point  $\pm 0.05$  mbar (p.221, l.26).

We did not observe any pressure fluctuations that follow the rotation frequency of the peristaltic pumps.

We changed this paragraph to:

“Pressure at the gas side of the gas extraction module is indirectly regulated to  $700 \pm 20$  mbar by the internal electronic pressure regulator of the WS-CRDS, which primarily controls pressure in the sample cavity (EPC Proportional Control Valve,

C585

EPCA06SSVXAA, Parker Hannifin Corporation). This results in a pressure gradient of approximately 300 mbar across the hydrophobic membrane of the module, which is sufficient to extract all the air bubbles from the sample stream. Variations in the water-to-gas ratio in the sample stream as well as changes in the experimental setup (e.g. degradation of peristaltic pump tubing) introduce the observed pressure fluctuations of  $\pm 20$  mbar at the gas side of the gas extraction module. In this experimental setup pressure is kept constant only on the gas side: An additional pressure regulator on the water side of the gas extraction module could improve the stability of the gas extraction.”

3

*B. Vaughn: Referee #2 questions the 300 ppmv moisture level achieved with the Nafion drying system, which was measured by the WS-CRDS analyzer. It might be explained by the fact the analyzer may simply not be that well calibrated at this low end?*

Stowasser et al.: See answer to referee #2.

4

*B. Vaughn: Page 216, lines 17-18, typo/wording. “To prevent air reaches the gas extraction module...” should read “To prevent air from reaching the gas extraction module...”*

Stowasser et al.: Done.

C586

5

*B. Vaughn: Page 223, lines 4-5. To improve resolution, the pressure in the cavity was reduced from 225 mbar to 60 mbar. No mention is made if any tests were made to determine the optimum modified pressure. Could lower pressure work, or is this the practical limit. This might be useful to readers.*

Stowasser et al.: Lower pressure does work and has been tested since then (30 mbar). When the measurements were taken, only the 60 mbar had been tested. 60 mbar was a recommendation from the manufacturer.

We added a footnote on page 23, l.5:

“The reduced cavity pressure of 60 mbar was a recommendation of the manufacturer. Since then a reduced cavity pressure of 30 mbar was tested successfully with this instrument. It is noteworthy that the standard deviation of CH<sub>4</sub> mixing ratio measurements becomes worse with lower cavity pressure.”

6

*B. Vaughn: The plots in Figure 4 need labels for A & B. It would also help to explain that the green lines are the ice core measurements in 4A. Could better results be obtained by using a suite of CH<sub>4</sub> concentration standards so that the calibration sequence could end with air that would be closer to the value of samples (as determined from the most recently analyzed core)? Less ice might be lost to memory of the system?*

C587

Stowasser et al.: Labels added to Fig.4.

The green lines indicate ca. the last 2 thirds of each ice core measurement along 1.1m. The 1st third needs to be discarded since it takes ca. 10 minutes to remove all the standard gas molecules from the system. This is mentioned in the caption of Fig.4a.

Yes, less ice is lost when using standard gas with CH<sub>4</sub> mixing ratios close to the mixing ratios found in the ice. Two practical reasons prevented us from doing so:

- We deployed only two standard gas tanks to the field. One of them with CH<sub>4</sub> mixing ratios close to glacial values and one close to interglacial values.
- We like to see a clear step from standard gas measurements to ice core measurements to be able to clearly identify each run in our daily data files. Thus, the CH<sub>4</sub> mixing ratios of the standard gases should not be too close the ones found in the ice core.

7

*B. Vaughn: Figure 7C could be improved by giving the two different transfer functions different symbols or colors so the reader could readily discern between original and modified analyzer.*

Stowasser et al.: Done.

---

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 211, 2012.

C588